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Ignition of Flammable Gases in Crude-Oil Tankers as a Result of Metal Fracture

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A literature search and an energy analysis have shown that the energies generated and the temperatures developed by metal fracture are not sufficient to ignite a flammable mixture of hydrocarbon vapor and air directly. It was concluded from this study that if metal fracture were to be a cause of ignition, it would be by an indirect process. The most likely cause of ignition resulting from metal fracture would be due to frictional impact or friction of fractured metal structural members with each other or with other objects. It was also concluded that

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normal impact (without friction) or single rubbings would not generate sufficient energy for ignition unless friction sparks also resulted. Friction sparks are more likely to cause ignition if highly pyrophoric metals are present. It was also concluded that adiabatic compression is a possible source of ignition in the case of ship collisions. It is felt that a further detailed study of this subject is not necessary.

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IGNITION OF FLAMMABLE GASES IN CRUDE-OIL TANKERS AS A RESULT OF METAL FRACTURE

INTRODUCTION

As a result of several unexplained explosions in some of their crude-oil tankers, an Italian classification society (RINA) raised certain questions concerning the possibility that these and similar explosions may have been caused by ignition due to local heat developed "either by initiation and propagation of a crack or by the rubbing of cracked surfaces" in metal structural members of the ship [1]. To obtain assistance in answering these questions, they requested information from the U.S. Coast Guard concerning the latter's experience and opinions on the possibility of the ignition of flammable vapors by metal fracture or other related ignition sources.

Because these questions bear on the important subject of ship safety, the Coast Guard sought additional opinions from NRL, NASA, and others who might have special knowledge in this area. Mr. R.W. Judy, Jr., of the NRL Engineering Materials Division made a brief analysis of the energies released and the temperatures involved in metal fracture [2], and he concluded that the "possibility of igniting a flammable gas or liquid by the action of the initiation or propagation of a fracture of a containing vessel fabricated from ordinary mild steel is remote, at best." These preliminary calculations indicated that the energy released by metal fracture is insufficient to ignite a flammable vapor-air mixture by itself. However ignition by a secondary process, such as by impact or rubbing of the fragments resulting from the fracture with each other or with some other body, appeared feasible.

Because of the important implications of these questions on the hazards of transportation of flammable liquids and gases, particularly in large ocean-going tankers [3-5], the Coast Guard decided to probe further into this subject. NRL was requested to make a feasibility study regarding the need, if any, for a detailed investigation of ignition of flammable gas mixtures by metal fracture. The NRL study, it was agreed, would be limited to a search of available scientific literature on ignition and related areas and to an analysis of the energies generated and temperatures developed by metal fracture. It was anticipated that no experimental work would be necessary in the NRL study.

IGNITION OF FLAMMABLE VAPORS

People in a wide variety of activities have always had a great interest in the ignition of flammable vapors and gases. These include people involved in the manufacture, transportation, handling, or storage of large quantities of flammable liquids and gases or those concerned with safety in potentially flammable atmospheres such as in coal mines. These would include petroleum refiners, manufacturers of solvents, the military, regulatory bodies,

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railroads, the trucking industry, and the U.S. Bureau of Mines. The great bulk of the work on ignition of flammable gases and vapors by impact and friction have been done by researchers concerned with safety in coal mines, mainly in the United States and Great Britain [6-10].

Two requirements must be met before a mixture of a flammable gas with air will ignite. First, the relative proportions of the gas and air in the mixture must be within certain flammability limits. Second, there must be an ignition source of sufficient energy to initiate flame propagation in the mixture [4]. Only if both of these requirements are met will ignition occur. For this study our concern is only with possible ignition sources, so that it will be assumed that all vapor mixtures under consideration are flammable, that is, within the flammability limits. Our only interest will be whether there is an ignition source of sufficient energy to ignite a flammable gas mixture.

Since our focus is on metal fracture as a direct or indirect ignition source, further simplifications may be made. As suggested by Burgoyne [4], the numerous possible sources of ignition may be divided into two classes based on the manner in which the ignition occurs. Ignition may occur "spontaneously" throughout the volume of the gas mixture due to the conditions of the temperature prevailing throughout the mixture. This type of ignition, in which no external ignition source is applied, is called *spontaneous ignition* or *autoignition*. Ignition can also occur locally from a small source of energy such as a flame, spark, or hot surface and then propagate from the source throughout the relatively cool mixture.

Local ignition sources can include open flames, electric sparks or arcs (including electrostatic discharges), hot electric wires or filaments, friction sparks, and other types of heated surfaces. We are interested only in ignition by local heat sources, such as might result from fracture, impact, or friction. We will therefore not be concerned in any detail with spontaneous ignition or the other ignition sources which have been enumerated, with one possible exception. This exception involves a combination of static electricity and the freshly exposed metal surface resulting from a fracture. If an electrostatic charge were to build up in the oil as a result of sloshing about in the tank, it might discharge to the exposed metal surface as an electric spark. A high-voltage spark is of course capable of igniting flammable vapors.

IGNITION BY HEATED SURFACES

If a heated surface such as a hot metal strip or other object is immersed in a flammable gas mixture, ignition may or may not occur depending on its temperature and size and how long it is immersed. Any body which is hot enough can ignite a flammable mixture. This does not depend on how it has been heated initially, whether by direct application of a flame, by conversion of electrical energy to heat, or by conversion of mechanical energy (fracture, impact, or friction) to heat.

An estimate of the temperature of an object which has been heated by mechanical means (such as by fracture) can be calculated, but prior to this calculation it would be useful to have an idea as to the magnitude of the temperatures which are required for hot-surface ignition.

The minimum temperature at which a hot surface will ignite a flammable mixture depends on the composition of the mixture (both the nature and concentration of the combustible) and on the size (geometry and area) and the nature of the surface. As pointed out by Burgoyne [4], "If a local source of heat is immersed in a gas mixture, convection currents are set up which cause the mixture to flow upward past the hot source." Because of the resulting temperature differences between the source and the gas, and the temperature gradients in the gas itself, the "source temperature for ignition of the gas will be high compared with its spontaneous-ignition temperature, and particularly so as the source is made smaller." If we assume that we are dealing with hydrocarbon vapors (as in the case of the ullage space of a crude oil tanker at ambient temperatures), these will consist chiefly of "light end" components depending on the source of the crude oil and the temperature. Spontaneous-ignition temperatures of hydrocarbons vary with chemical structure, composition, and how they are determined, but certain generalizations may be made [4,11,12]. Spontaneous-ignition temperatures (SIT) for the n-alkanes vary inversely with chain length from about 562°C for methane down to about 202°C for the higher alkanes (tetradecane on up) [12]. Branched and aromatic hydrocarbons exhibit higher spontaneous ignition temperatures. For example the spontaneous ignition temperature of 2,2-dimethyl butane (a hexane isomer) is 405°C and that of benzene is 548°C [11]. Temperatures required for hot-surface ignition, as was pointed out, would be expected to range far above these temperatures. For example, hot-surface-ignition temperatures for methane (SIT = 562°C) were found to vary from above 1000°C to 1600°C, depending on the size of the ignition sources [4,6]. From these and similar data, it is apparent that even in the relatively unlikely possibility that the vapor composition consisted of higher n-alkanes, the minimum hot-surface ignition would be expected to be well above the spontaneous-ignition temperature of 202°C. The vapor composition even at high ambient temperatures would consist of shorter chain hydrocarbons, with higher spontaneous-ignition temperatures.

ANALYSIS OF ENERGY RELEASE BY METAL FRACTURE

A great amount of stored energy is released when a large structural element such as a strake in a ship fractures in a brittle manner, and this automatically makes fracture a suspected source of ignition. A search of the literature did not reveal any evidence that metal fracture by itself could be a source of ignition for hydrocarbon vapors in air. Titman [9] reported ignitions of hydrogen in air by high-speed impact of a steel ball on lead targets when the ball broke up in the target, and no ignitions were found when breakup did not occur. Titman stated that these ignitions were unexpected and were invariably associated with breakup of the ball in the target. Ignition was not obtained when the ball did not break, and this suggests, he postulated, that the primary cause of ignition was the breaking of the ball. This was confirmed [9] by breaking steel balls with a hammer blow in a flammable atmosphere. He found that hydrogen-air mixtures were frequently ignited, but ignition did not occur when the same experiment was repeated with methane-air and pentane-air mixtures. A possible ignition may have occurred in the same experiments with methane in oxygen-enriched atmospheres.

It was therefore decided to make an analysis of the energies released and the temperatures developed by metal fracture for comparison with hot-surface-ignition temperatures of hydrocarbons.

Fracture Mode and Local Heating

Unstable Crack Extension

The types of steels conventionally used for ship construction can fracture by means of two different metallurgical modes of separation. One is a brittle mode (cleavage), and the other is a ductile mode (microvoid coalescence). These fracture modes are temperature dependent, and when the temperature of the steel drops below 15°C the potential for cleavage fracture increases. At −18°C (0°F) the fracture mode of as-rolled ship plate is predominately by cleavage.

The speed at which fractures propagate is mode dependent, and when the fracture mode is more than 75% cleavage, cracks are self-propagating (unstable) and travel at 0.3 to 1 km/s. When the fracture mode is predominately ductile, less than 50% cleavage, cracks in ships are generally no longer unstable. Under these conditions, fractures propagate only as fast as the overload system tears the plate apart.

Stable Crack Extension

Cracks can propagate slowly by several mechanisms. Under normal service conditions the crack remains stable, but it can grow at small increments until repair is necessary. The most common mechanisms for slow stable crack growth are by a fatigue mechanism or by stress-corrosion cracking. The latter mechanism requires liquid to be present in the crack, and, due to the slow growth rate associated with stress-corrosion cracking, no local elevation in temperature occurs. Therefore stress-corrosion cracking can be discounted as a potential source of ignition.

Separation by a fatigue mechanism can also be discounted as a potential source of ignition, because only a small amount of local energy is involved per cycle of load, and it is dissipated over a relatively long period of time. For example a fast propagation rate for low-cycle fatigue cracking is 0.025 mm per cycle, and any normal cyclic load would be too slow to cause any significant elevation in temperature at the crack tip. Since only ambient temperatures exist at the tips of cracks extending by stable-crack-growth mechanisms, these fracture mechanisms are not potential sources for ignition.

Fast Fracture and Local Heating

The energy required to fracture a section of ship steel is directly related to the strength level and plastic strain associated with the fracture mechanism. Since the strain associated with fracture is at a maximum when the steel fractures in a ductile mode, a simple adiabatic thermal analysis can predict the potential temperature rise due to fraction. For the parameters of a conventional ship steel, the elevation in temperature under the most favorable conditions of heating due to fracture energy can be calculated as follows. Let

S_y = av yield strength (35,000 psi = 241 MPa = 241 MN/m^2),

S_u = av tensile strength (65,000 psi = 448 MPa = 448 MN/m^2),

El = elongation during fracture (50% = 0.50),

C = heat capacity of steel (0.116 BTU/lb °F = 486 J/kg °C),

d = density of steel (7750 kg/m^3).

The work to fracture 1 m^3 of steel is

$$\begin{aligned} W &= [(S_y + S_u)/2]El \\ &= 172\ MN\ m/m^3, \end{aligned}$$

and, since 1 Nm = 1 J, the heat eqivalent Q of the mechanical energy of fracture is

$$Q = 172\ MJ/m^3.$$

Then the temperature elevation due to fracture is

$$\begin{aligned} \Delta T &= Q/Cd \\ &= (172 \times 10^6\ J/m^3)/(486\ J/kg\ ^\circ\mathrm{C})(7750\ kg/m^3) \\ &= 46^\circ\mathrm{C}. \end{aligned}$$

The temperature rise associated with fractures can also be calculated using the fracture mechanics parameter G_c, which is the strain energy release rate per unit area of fracture surface. The highest value for G_c associated with brittle unstable fracture in ship steels occurs when the plastic zone size ($2r_y$, where r_y is the radius) is equal to the thickness of the plate. The adiabatic temperature rise for a typical steel under these conditions (G_c = 1,000 in.-lb/in.^{2} when the plastic zone size $2r_y$ is 1 in., which converts to G_c = 175 kJ/m^2 when 2 r_y is 0.0254 m) is

$$\begin{aligned} \Delta T &= \frac{G_c}{2r_y}/Cd \\ &= \frac{175{,}000\ J/m^2}{0.0254\ m}/(486\ J/kg\ ^\circ\mathrm{C})(7750\ kg/m^3) \\ &= 1.8^\circ\mathrm{C}. \end{aligned}$$

Metal Fracture as a Direct Source of Ignition

It would thus appear from the results of the preceding calculations that the energy directly associated with the fracture of ship steel would be too small to cause the fractured surfaces to increase in temperature sufficiently to cause ignition. Even in the case of a collision causing a ductile-fracture tearing situation, the local temperature rise would be significantly less than 56°C (100°F) without the heat of friction or abrasion. If we assume an extreme case of an ambient temperature of about 88°C (190°F), which might occur in the ullage space of a tanker in tropical waters, a temperature increase of 56°C (100°F) would result in a temperature of 144°C. As discussed previously, this temperature is well below the minimum autoignition temperature of hydrocarbon vapors. If brittle fracture occurred, the temperature rise of the steel associated with the fracture would be less than 6°C (10°F).

Metal Fracture and Exposure of Pyrophoric Microparticles

Some microconstituents may be considered to be pyrophoric under certain conditions. For example some inclusion or thin iron splinter could ignite when it became exposed to air at the crack tip. The question is whether the size conditions are sufficient to be of concern for ignition.

Except for large slag inclusions, which are chemically inert, the inclusions in steel are complex reaction products of oxygen, sulfur, carbon, and additives such as the rare earth metals, aluminum, calcium, titanium, and magnesium. These inclusions are small, less than 0.025 mm, and even if they are active chemically, little energy would be involved. Furthermore the size of the opening when the crack front extends is also small. This opening can be calculated on the basis of fracture mechanics using the relationship

$$COD \approx G_c \sigma_{ys}$$

where *COD* is the crack opening displacement and σ_{ys} is the stress at yield-strength level. For the case of brittle fractures, the *COD* is of the order of 0.2 mm. For the case of a ductile fracture, the *COD* is of the order of 0.5 mm. Any pyrophoric particle that became exposed to air at the crack tip would be consumed before the *COD* would be significantly larger than these values. Flame propagation is suppressed in narrow spaces, and if the space is narrow enough, a flame will be quenched. Depending on the experimental method used to determine the "minimum quenching distance" (MQD) or the "maximum experimental safe gap" (MESG), slightly different data are obtained. For hydrocarbons in air at atmospheric pressure, the MQD is about 1.5 to 2 mm [4,13], and the MESG is about 0.7 to 1.2 mm [4,14]. Since the *COD* associated with either brittle or ductile fracture in ship steel is small, it would thus act as a flame arrester even if a pyrophoric particle were present. Therefore it does not appear that pyrophoric particles in steel can be potential sources for ignition by fracture. Ignition by pyrophoric metals will be discussed further in the next section.

METAL FRACTURE AS AN INDIRECT SOURCE OF IGNITION

Although metal fracture by itself is not likely to ignite a flammable gas mixture, the question arises as to whether metal fracture might be an indirect source of ignition. What if fractured fragments rub against one another? What if fragments impact on other surfaces? Would sparks be generated as a result of such impact or friction? Would heat produced by impact or friction be sufficient to ignite flammable gases? These questions are an important part of this problem.

Ignition as a Result of Friction and/or Frictional Impact

During normal or collision impact, in which the impacting forces have no tangential component, and in which friction plays no part, the heat produced by plastic deformation is dissipated throughout the volume of the deformed material [6,7]. Measurements show that the surface temperature increases only a few degrees as a result of such impact [6,7]. On the other hand, impact accompanied by friction ("oblique impact") can cause ignition under suitable conditions [4,6,7]. When mechanical energy is expended in doing work against friction, the energy dissipated is transformed into heat at the rubbing surfaces [6]. The limiting temperatures reached can approach the lower of the melting points of the two rubbing materials [6,7]. For this reason abrasion of two rocks may result in higher surface temperatures and more sparks than would result from rubbing two metals. Nevertheless numerous examples of ignitions of methane-air mixtures by rubbing or frictional impact of two steels are given by Powell [6], Hartman [8], and Titman [9] in their reviews on this subject. However ignitions were difficult to achieve, and sparking was usually necessary. Ignition was obtained more readily when one of the metal surfaces was rusty [6].

Ignition by Frictional Sparks from Pyrophoric Metal Particles

In the previous discussion on ignition by friction or frictional impact, the mechanism of ignition involved local heating of a small volume of the gas mixture by direct contact with a hot surface which had been heated by rubbing. Another source of friction ignition is when small heated particles are torn off from the rubbing metal and projected into the mixture, either as inert hot particles or as actively oxidizing particles (friction sparks) whose temperatures have been augmented by oxidation. The ability of friction sparks to ignite flammable mixtures will depend on the nature, size, and temperature of the burning particles and the length of time of its contact with the gas [8-10].

The ability of different metals to ignite flammable gases varies from metal to metal, depending on their heats of oxidation and other factors [10,15,16]. Certain metals such as thorium, cerium, zirconium, titanium, magnesium, and aluminum are particularly effective in causing friction-spark ignition [10,15,16] and are referred to as *pyrophoric* metals. Their ability to form friction sparks (referred to as *pyrophoricity*) is based on the fact that the fragmented particles ignite spontaneously with air, and it is these burning particles which can ignite a flammable gas mixture. Cerium, for example, is the major constituent of a cigarette-lighter flint [16].

The question now is raised, if friction and/or impact resulting from metal fracture should occur on a tanker, will sparks be formed of sufficient energy to ignite a flammable gas mixture? Are there any pyrophoric metals in the steel members of a tanker? As mentioned previously, steel includes small amounts of pyrophoric metals such as titanium. Smaller amounts of other pyrophores may also be present. The steel in a tanker however is often coated with different types of zinc coatings [17]. Since zinc is not pyrophoric [8,9,16], it is not likely to be a spark-ignition source in the case of a single impact or rubbing. However, in the case of continuous rubbing, the exposed metal beneath the zinc coating might result in spark ignition because of the presence of these pyrophoric materials.

Ignition by Frictional Impact and/or Friction of Aluminum Alloys and Rusted Steel ("Thermite" reaction)

Although aluminum alloys are not likely for tanker use, the hazard of a reaction between aluminum and rust ("thermite" reaction) is important enough to mention briefly because of the possibility of using aluminum paint on a rusted steel surface. If a light metal such as aluminum strikes an oxidized steel surface, the heat of rubbing may initiate a "thermite" reaction between the aluminum and the iron oxide. This high-temperature reaction can in turn ignite the metal particles rubbed off by the friction [4,18]. If aluminum is smeared onto a rusted surface, an impact on this mixture of light metal and rust may emit high-temperature sparks, and this could ignite a flammable atmosphere.

Ignition Resulting from Ship Collisions

A study was made recently [19] of explosions resulting from ship accidents, chiefly involving "penetration collisions." Although the major interest in this 25-year statistical study was concerned with LPG cargos, its study included other liquid hydrocarbon fuels. It was found that in about 95% of the penetration-collision accidents, explosions occured as long as the ambient temperature was above that of the flash point of the fuel cargo. It was estimated from photographs and actual examinations of the welds resulting from the heat due to scraping of the metal surfaces in the collision that temperatures exceeded 770°C. In many cases sparks were reported during the collision. Ignition of flammable vapors could easily result under these conditions. Some ignitions were reported to be due to rupture of electrical cables and similar causes. The conclusion was that ignition was not due to impact alone but involved friction and other energy sources.

Ignition Resulting from Adiabatic Compression

Another possible ignition source during a collision involving penetration is adiabatic compression. If the ullage space in a tanker is suddenly compressed, temperatures would increase rapidly and, as shown by Burgoyne [4], could become high enough to cause ignition. If the compression is rapid, shock waves could result, which would cause even higher temperature increases. A recent paper [3] reported experiments to record the pressures caused by the slamming of ballast water against tank walls in partly filled holds to determine whether the pressures attained could exceed the ignition temperatures of the vapors present. The results were inconclusive, but the data suggested that compression ignition cannot be discounted.

IGNITION BY STATIC ELECTRICITY

As mentioned earlier, a combination of static electricity and metal fracture of a ship's structural member might cause an ignition in an oil tanker. The sloshing of oil or oily water (ballast) due to the roll of the ship can cause a buildup of electrostatic charge [3]. Low-energy sparks from oil-water sloshing have been observed on oil-bulk-ore tankers, but, as might be expected, the charge was low due to such relatively mild motion, [3].

The question arises as to whether a fracture of a ship's structural member might increase the hazard of spark ignition. Because the fracture creates a freshly exposed surface, it might be conjectured that the low electrical resistance of the clean surface (particularly if the fracture causes a fragment to separate and close the gap to the liquid surface) might concentrate the field and thus cause an ignition. This is not considered a likely source of ignition, however, since the charge due to sloshing is low. Furthermore, as the charge builds up, charge relaxation simultaneously occurs to the walls of the tank. Therefore the electrostatic spark discharges under these conditions are not likely to be of sufficient energy to ignite a flammable gas mixture [20], even if the field is concentrated at the fractured surfaces.

SUMMARY AND CONCLUSIONS

A literature search and an energy analysis have been made to ascertain whether the energies generated and the temperatures developed by metal fracture might be a possible cause of ignition of flammable atmospheres on a crude-oil tanker. It was concluded that the temperatures developed by metal fracture were not sufficient to ignite a flammable hydrocarbon-air mixture directly.

It is considered that if metal fracture were to be a cause of ignition, it would be by an indirect process. The most likely cause of ignition resulting from metal fracture would be due to frictional impact or friction of the fractured metal structural members with each other or with other objects. It was concluded that normal impact (without friction) would not cause sufficiently high temperatures to cause an ignition, so that only impact accompanied by friction should be considered. Single-rubbings or single frictional impacts would not generate sufficient energy for ignition unless friction sparks also resulted. Friction sparks are more likely to cause ignition if highly pyrophoric metals are present. Explosions due to ship collisions may be due to a variety of causes, but in the case of penetration collisions the ignition source would not be due to normal impact but rather would be due to energy released by friction. Adiabatic compression is a possible source of ignition in the case of ship collisions. Ignition due to a combination of metal fracture and static electricity is not likely.

It is concluded that fracture of a steel structural member of an oil tanker or similar type of ship is not likely to ignite a flammable mixture of hydrocarbon vapor and air either directly or indirectly.

It is felt that a further detailed study of this subject is not necessary.

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